The Photovoltaic Performance of CdS/Cu$_2$S (QD) Co-Sensitized Solar Cell


*a,b,c Mathematal and Physical Engineering Department, Faculty of Engineering (Shoubra), Banha University, Cairo, Egypt
dPhysics Department, Faculty of Science, Benha University, Cairo, Egypt
fPhysics Department, Faculty of Science, Ain Shams University, Cairo, Egypt

*Email: akh_ghalia@yahoo.com
bEmail: dr_easawi@yahoo.com
cEmail: dr.saiedabdallah@yahoo.com
dEmail: merfat.alsharawy@fsc.bu.edu.eg
eEmail: drnegm@hotmail.com
fEmail: hassantalaat@hotmail.com

Abstract

The performance of CdS/Cu$_2$S co-sensitized quantum dot solar cell (QDSSCs) is studied. CdS quantum dots (QDs) were adsorbed onto TiO$_2$ using Successive Ionic Layer Adsorption and Reaction (SILAR) method for different cycles (2, 4, 6, 8 and 10). The Cu$_2$S QDs were deposited onto TiO$_2$/CdS10 cycle photoanodes using the same method. The FTO counter electrodes were coated with platinum, while the electrolyte containing polysulfide redox species was sandwiched between the two electrodes. The current density-voltage (J-V) characteristic curves of the assembled QDSSCs were measured at different cycles and AM 1.5 simulated sunlight. The value of current density ($J_{sc}$) and conversion efficiency (η) of TiO$_2$/CdS/Cu$_2$S are 252% larger than the TiO$_2$/CdS values. The maximum values of $J_{sc}$ and η are 3.56 mA/cm$^2$ and 1.21% respectively corresponding to CdS10/Cu$_2$S for 6 cycles of Cu$_2$S.

Keywords: Quantum dot sensitized solar cell (QDSSCs); CdS QD; SILAR; photovoltaic parameters.

* Corresponding author.
1. Introduction

In the last two decades, a great effort has been indicate to improve of the performance of the third generation solar cells, especially that of quantum dots sensitized solar cells (QDSSCs) [1]. In this kind of solar cells, quantum dots (QDs) are adsorbed onto a large band gap metal oxides such as TiO_2 nanoparticles (NPs) [2-7], ZnO NPs [7-11], and SnO_2 NPs [7] to act as light more harvesting sensitizers [12]. These QDs possess many attractive properties such as the ability to tunable band gaps, high absorption coefficients due to quantum confinement, large dipole moment leading to rapid charge separation and as well low manufacturing cost [13]. CdS has become a very attractive promising material for many specific applications in solar energy conversation and Cu_2S is highlighted because of its non-toxic, low cost and earth-abundant properties. The band-gap of bulk Cu_2S is 1.20 eV, which can make Cu_2S become a widely used photosensitizer for various wide band-gap semiconductor photoanodes [14]. The adsorbing of Cu_2S QDs onto TiO_2/CdS can make TiO_2/CdS/Cu_2S which would be more efficient for solar energy utilization than single semiconductor doped one. Their band gap matching for solar light absorption along wide band gap tenability and high absorption coefficient [15]. Synthesizing QDs techniques may involve different scientific processes, such as chemical, physical, biological, or some combination of these processes [16]. In some chemical methods, QDs are synthesized either by chemical bath deposition (CBD) technique or successive ionic layer adsorption and reaction (SILAR) method [16]. In our study we use SILAR, since it is simply adjusted by controlling the number of deposition cycles. A. Badawi and his colleagues employed CdSe QDs sensitized TiO_2 using the direct adsorption technique (DA) to anchor CdSe QD onto TiO_2 substrate and the efficiency for energy conversion $\eta$ has been increased from 0.11 % to 0.29 % [9]. N. Al-Hosiny and his colleagues studied CdTexS_{1-x} QDs to deposit TiO_2 mesoporous, they tuned the efficiency via molar ratio control of CdTexS_{1-x} QD and reported the maximum value of $\eta$ was 0.31 % for $x=0.6$ of CdTexS_{1-x} [10]. In our work CdS QDs and CdS/Cu_2S QDs were adsorbed onto the surface of the TiO_2 electrode by (SILAR) method. The effect of the CdS QDs and CdS/Cu_2S QDs number SILAR cycle on the QDSSCs photovoltaic parameter (short circuit current density $J_{sc}$, open circuit voltage $V_{oc}$, fill factor FF, efficiency for energy conversion $\eta$) has been investigated.

2. Experimental

2.1. Deposition of the CdS QDs onto TiO_2 NPs photoanode

The nano TiO_2 paste was prepared by the following procedure of G. Syrrokostas et.al [17]. The CdS QDs were sensitized onto TiO_2 nanoparticles using SILAR method [18]. The photoanode is immersed for one min in 0.1 M (Cd(NO_3)_2.H_2O) in methanol as a cation source (Cd^{2+}) and to be adsorbed on the TiO_2 electrode. The TiO_2 electrode was then rinsed with methanol to remove the excess Cd^{2+} cations. Then the photoanode is immersed in 0.1 M Na_2S methanolic solution as the anion source (S^{2-}) for one min in order to react with Cd^{2+} cations followed by methanol rinsing. This procedure was referred to as one SILAR cycle. Five samples obtained at increasing number of cycles labeled a, b, c, d and e for 2, 4, 6, 8 and 10 cycles, respectively. The counter electrodes were prepared by coating another Florien-doped Tin Oxide (FTO) substrate of resistance of 7 $\Omega$/sq.
with platinum (Pt).

2.2. Deposition of the Cu₂S QDs onto TiO₂/CdS10 QDs photoanode

In this part, the Cu₂S QDs were deposited onto TiO₂/CdS10 (sample e which has high efficiency) by the same method (SILAR technique). The photoanode is immersed for 1 min in 0.1 M (CuNO₃)₂.4H₂O in methanol as a cation source (Cu⁺²) and to be adsorbed on the TiO₂ electrode. The TiO₂ electrode was then rinsed with methanol to remove the excess Cu⁺² cations. Then the photoanode is immersed in 0.1 M Na₂S methanolic solution as the anion source (S⁻²) for 1 min in order to react with Cu⁺² cations followed by methanol rinsing. We get also five samples at different cycles labeled a, b, c, d and e for 2, 4, 6, 8 and 10 cycles respectively.

2.3. Assembly of QDSSCs

QDSSCs were built by assembling the TiO₂ photoanodes sensitized with (CdS and CdS/Cu₂S), aqueous polysulfide electrolyte and the counter electrodes. Parafilm was used as spacer between the two electrodes and also as a sealing to prevent the evaporation of the electrolyte. The space between the two electrodes was filled by polysulfide electrolyte which was prepared by dissolving 1.1M Na₂S, 1.2 M S, and 0.12 M KCl in deionized water [19].

2.4. Characterizations and measurements

The UV-Vis absorption spectra were recorded using (Jasco 670 with 1cm quartz cuvettes) spectrophotometer. The size and morphology was determined using high resolution transmission electron microscopy (HRTEM, JEOL JEM-2100 operated at 200KV with high resolution Gatan CCD bottom camera, Orius SC200). Photovoltaic solar cell measurements were performed using a solar simulator device (San-Ei Electric XES-40S1) at AM 1.5 with 1 sun illumination intensity (100 mW/cm²), and current density–voltage (J–V) data were recorded using a source meter unit (Keithley SMU 2600).

3. Results and Discussion

3.1. Optical measurements of CdS QD

For TEM measurement, TiO₂/CdS layer in ethanol was scratched from FTO coated substrate without disturbing FTO layer and placed on Cu-coated carbon grid. Figure 1 shows the TEM image of TiO₂/CdS for sample (e). The average particle size for CdS QD were estimated to be approximately 5.4 nm and average particle size for TiO₂ is 22 nm.

Figure 2 show UV-visible absorption spectra for (TiO₂ and TiO₂ / CdS layer with increasing number of cycles by SILAR method). It can be seen that the TiO₂ layer shows an absorbance edge at 400 nm corresponding to 3.1 eV band gap. Also, there is a blue shift of absorbance edge with decreasing number of cycle. These are 401 nm, 414 nm, 431 nm, 451 nm and 465 nm for samples (a, b, c, d and e) respectively. This blue shift is due to quantum confinement effect [20].
Figure 1: TEM image of TiO$_2$ / CdS QD for sample (e)

Figure 2: Show UV-vis absorption of TiO$_2$/CdS QD electrode with different number of cycles by SILAR method.

The particle size of CdS QD is calculated using the effective mass approximation (EMA) model [21-23].

$$ E_{gn}(R) = E_{gb} + \frac{\hbar^2}{8m^*R^2} - \frac{1.8e^2}{4\pi\varepsilon_0R} $$

where $E_{gb}$ (2.4 eV) is the bulk band gap [21], $E_{gn}$ is the nano band gap, $R$ is the radius of the CdS quantum dots, $m^*$ ($7.62 \times 10^{-32}$ kg) is the reduced mass [21], and $\varepsilon$ (7.1) is the dielectric constant for CdS [21]. The average particle sizes of CdS QDs are obtained from UV.spectra and applied equation 1. The obtained values of CdS particle sizes ranged from 3.2 nm for sample (a) to 4.4 nm for sample (e) in close agreement with that...
obtained by TEM measurements. The elemental analyses of the CdS QDs sensitized TiO$_2$ working electrode was measured using (EDX) (model JEOL JED-2300). Figure 3 shows the EDX spectra of TiO$_2$/CdS QDs sensitized working electrode where Cd, S, Ti and O atoms are indicated. This result ensures the adsorption of CdS QDs onto the TiO$_2$ electrode.

Figure 3: EDX of TiO$_2$/CdS QD working electrode for sample e

### 3.2. Photovoltaic performance of CdS QDSSCs

Figure 4.a shows the J-V characteristics curves of CdS QDSSCs measured under a simulated sunlight with an intensity of 100 mW/cm$^2$ (AM 1.5G). The value of $J_{sc}$ vs number of SILAR cycle of CdS QD are shown in Figure 4.b. The photovoltaic parameters $V_{oc}$,$J_{sc}$, FF and $\eta$ for produced CdS QDSSCs are given in Table 1. It is clearly seen that as CdS QDs size increases, the values of $J_{sc}$ and $\eta$ increase. The maximum values of $J_{sc}$ and $\eta$ are 2.24 mA/cm$^2$ and 0.48% respectively for 10 cycles (sample e) of CdS QD. S.Abdallah et. al [24,25] has made measurement on CdS QD sensitized TiO$_2$ using the direct adsorption technique (DA) to anchor CdS QD onto TiO$_2$ substrate. They reported that, there are an increase of $J_{sc}$ (from 0.31 mA/cm$^2$ to 0.67 mA/cm$^2$) and $\eta$ (from 0.05% to 0.18%) as the CdS particle size increase. Our results shows that an increase of $J_{sc}$ (from 1.18 mA/cm$^2$ to 2.24 mA/cm$^2$) and $\eta$ increase (from 0.15 to 0.48) with increasing particle size of CdS QDs in agreement with their work. They attributed the increase in $J_{sc}$ with increase particle size in a red shift and thus causes relativity high absorption of the incident photon from solar spectrum. Therefore, particle size of CdS QD 4.4 nm (correspond to 465 nm) harvest more visible photon than the other particle. However, our results show an improvement of the $J_{sc}$ and ($\eta$) than their work by 266% which may be due to the SILAR technique is being better method than DA technique to give high-quality surface spread, lower aggregation, higher photocurrents, longer lifetimes of electron and solve problem of surface chemistry which lead to improve QDSSCs [26].

Figure 4.a: J-V characteristic curve of QDSSCs of CdS QDs with different size (different cycle)
Figure 4.b: Variation of the current density as a function of SILAR cycles of CdS QD

Table 1: J -V characteristics parameters of a CdS QDSSCs for different QDs sizes, under 1 sun illumination.

<table>
<thead>
<tr>
<th>Sample</th>
<th>V&lt;sub&gt;oc&lt;/sub&gt; (m Volt) ± 0.01</th>
<th>J&lt;sub&gt;sc&lt;/sub&gt; (mA/cm&lt;sup&gt;2&lt;/sup&gt;) ± 0.01</th>
<th>FF</th>
<th>η(%) ± 0.01</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO&lt;sub&gt;2&lt;/sub&gt;/CdS</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a</td>
<td>508</td>
<td>1.18 ± 0.01</td>
<td>0.24</td>
<td>0.15</td>
</tr>
<tr>
<td>b</td>
<td>505</td>
<td>1.38 ± 0.02</td>
<td>0.35</td>
<td>0.24</td>
</tr>
<tr>
<td>c</td>
<td>504</td>
<td>1.82 ± 0.01</td>
<td>0.39</td>
<td>0.37</td>
</tr>
<tr>
<td>d</td>
<td>509</td>
<td>2.01 ± 0.01</td>
<td>0.38</td>
<td>0.42</td>
</tr>
<tr>
<td>e</td>
<td>510</td>
<td>2.24 ± 0.01</td>
<td>0.40</td>
<td>0.48</td>
</tr>
</tbody>
</table>

3.3. Optical measurements of CdS10/Cu2S QD

In this part, the Cu<sub>2</sub>S QDs were deposited onto TiO<sub>2</sub>/CdS(10) photoanodes by SILAR method (which has higher J<sub>sc</sub> and η). Figure 5 shows the UV spectra of TiO<sub>2</sub>/CdS10/Cu2S photanode for different number of cycle. The absorption edges varies between 487 nm for sample a with a corresponding band gap of 2.55 eV to 553 nm for sample e with a corresponding band gap of 2.24 eV which should be ascribed to the contribution of Cu<sub>2</sub>S, since its band gap was reported to be 1.2 eV [15]. It was also noted that, the absorption intensity of this band gradually increased with the increasing amount of Cu<sub>2</sub>S in CdS.
Figure 5: show UV-vis. absorption of TO2/CdS10/Cu2S QD electrode with different number of cycles by SILAR method

3.4. Photovoltaic performance of CuS/CdS QDSSCs

Figure 6 shows the J-V characteristics curves of (CdS10/Cu2S) QDSSCs measured under a simulated sunlight with an intensity of 100 mW/cm² (AM 1.5G). The photovoltaic parameters (V.oc, I.sc, FF and η) for all the sample are obtained and given in Table 2.

It is clearly seen that as Cu$_2$S QDs SILAR cycles increases, the values of J.sc and η increases peaking at 4.01 mA/cm² and 1.21% respectively for 6 cycles (sample c) which about 252% larger than TiO$_2$/CdS. These values decrease for sample d (3.56 mA/cm² and 0.96%) and sample e (2.60 mA/cm² and 0.73%). The increase of J.sc and η can be explained by two effect. First effect, due to the relative narrow band gap of Cu$_2$S (1.2 ev) [15], Cu$_2$S can increase the utilization efficiency of the incident light, and result in the more efficient charge
separation in CdS QD, which can improve the transportation of the photosensitized electron and reduce the recombination of the photosensitized electron and hole, so the performance of the whole efficiency will be promoted in turn [27].

**Table 2:** J -V characteristics parameters of CdS10/ Cu2S QDSSCs for different QDs cycles, under 1 sun illumination.

<table>
<thead>
<tr>
<th>sample</th>
<th>$V_{oc}$ (mVolt) ± 0.01</th>
<th>$J_{sc}$ (mA/cm²) ± 0.01</th>
<th>FF</th>
<th>$\eta$(%) ± 0.01</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>520</td>
<td>3.01 ± 0.01</td>
<td>0.41</td>
<td>0.52</td>
</tr>
<tr>
<td>b</td>
<td>531</td>
<td>3.72 ± 0.02</td>
<td>0.40</td>
<td>1.06</td>
</tr>
<tr>
<td>c</td>
<td><strong>527</strong></td>
<td><strong>4.01 ± 0.03</strong></td>
<td><strong>0.49</strong></td>
<td><strong>1.21</strong></td>
</tr>
<tr>
<td>d</td>
<td>525</td>
<td>3.56 ± 0.01</td>
<td>0.48</td>
<td>0.96</td>
</tr>
<tr>
<td>e</td>
<td>527</td>
<td>2.60 ± 0.01</td>
<td>0.41</td>
<td>0.73</td>
</tr>
<tr>
<td>CdS10</td>
<td>510</td>
<td>2.24</td>
<td>0.42</td>
<td>0.48</td>
</tr>
</tbody>
</table>

**Figure 7.a:** Relative band positions of TiO$_2$, CdS and Cu$_2$S in bulk and ideal stepwise structure

**Figure 7.b:** Band edges for the efficient transport of the excited electrons and holes in TiO$_2$/CdS/Cu$_2$S photoelectrode
Second effect, when TiO2, CdS and Cu2S are in bulk. Their band gap are 3.2 eV, 2.25 eV and 1.20 eV, respectively can be seen in Figure 7.a. Therefore, their band gap cannot match well to provide a good path for the transportation of the electrons due to that the conductor band of Cu2S is lower than that of CdS, which inhibit the photosensitized electrons transport from the Cu2S to CdS [27]. When Cu2S nanoparticles were coated on the CdS QDs a great number of nanoscale heterostructure between the two semiconductors could be produced. The band gap alignment of TiO2 CdS / Cu2S has been reported by Y. Chen and his colleagues [15], as shown in Figure 7.b. It is easily observed that the conduction band (CB) of CdS is lower than (CB) of Cu2S lead to the electron transfer occurred from Cu2S to CdS, and eventually to TiO2 [27]. While the hole transfer occurred from TiO2 to CdS and then from CdS to Cu2S due to the different Fermi levels alignment when the system reached equilibration state. And when the Cu2S SILAR reached 6 cycles, the interaction between Cu2S and CdS achieved the best effect. Our result show the increase of Jsc from 2 cycle (Sample a) 3.01 mA cm² to 6 cycle (sample c) 4.01 mA cm² support this argument. The decrease of Jsc for sample d and e are attributed to beyond 6 cycle CdS QD nearly covered by Cu2S nanoparticles, which would reduce the formation of more heterostructure and affect the efficient utilization of light by CdS nanoparticles. Additionally, the increase of Cu2S cycles led to an increase in the thickness which takes a longer time for the electron to reach the TiO2. Therefore, the probability of recombination or trapping of the generated holes would be higher, causing the photocurrent to decrease [28].

![Figure 8: Variation of the current density as function of SILAR cycles of Cu2S QD](image)

The value of $J_{sc}$ vs number of SILAR cycle of Cu2S QD is shown in Figure 8.

### 4. Conclusions

CdS QDs were adsorbed onto TiO2 nanoparticle electrode using SILAR method to act as sensitizer for QDSSCs. The absorption edges of TiO2/CdS photoanode are red shift as the number of cycle increases from 2 to 10. EDX measurements ensures the success of adsorption of CdS QDs onto the TiO2 electrode. The values of $J_{sc}$ and $\eta$ for CdS QDs solar cell increase as the number of cycle increase. Such an increase may be result from the
improving of photo-absorption efficiency and charge separation of TiO$_2$/CdS solar cell. Furthermore, Cu$_2$S were adsorbed onto TiO$_2$ / CdS (10) cycles (which has higher efficiency) with different cycles. The absorption edges of TiO$_2$/CdS10/Cu$_2$S photoanode are red shift from 487 nm to 553 nm as the number of cycle increases from 2 to 10 which should be ascribed to the contribution of Cu$_2$S. The maximum values of $J_{sc}$ (3.56 mA/cm$^2$) and $\eta$ (1.21%) are obtained for sample CdS10/Cu$_2$S for 6 cycles of Cu$_2$S which about 252% larger than TiO$_2$/CdS. The improvement of $J_{sc}$ and $\eta$ are due to the formation of heterostructure between CdS and Cu$_2$S which causes the conduction band (CB) of CdS is lower than (CB) of Cu$_2$S. Thus more electrons can be transfer from Cu$_2$S to CdS and injected to TiO$_2$ nanoparticle electrode.

Acknowledgements

The authors would like to express their sincere gratitude to Ain Shams University and the Physics Department at Ain Shams University for their financial and technical support in performing and finishing this work.

References


